

Functionalization of Recycled Diatomite for Green, Stable, and High-performance Phase Change Material (PCM) Composite

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Abstract. This study reports on the functionalization of recycled diatomite (DT) for preparing green and shape-stabilized phase change material (SSPCM); the DT-based SSPCM can be employed in HDPE composite for high latent heat and good thermal conductivity. After purification, the purified DT (P-DT) adsorbed polyethylene glycol (PEG) by the straight dipping process for producing SSPCM. P-DT showed high surface area of 58 m²g⁻¹ and low organic impurity (<1%); the PEG/P-DT SSPCM exhibited high latent heat of 45 Jg⁻¹ and low leakage (<0.3%). By adding PEG/P-DT SSPCM into the HDPE, the SSPCM/HDPE composite improved both the heat deflection temperature (HDT) and maximum decomposition temperature (T_{max}) to 89.18°C and 500.2°C, respectively. In seeking to enhance tensile strength and thermal conductivity, maleated polyethylene (MAPE) and alumina (Al₂O₃) were studied in the SSPCM/HDPE composite. In the end, the SSPCM/HDPE composite exhibited great heat resistance, mechanical property and thermal conductivity.

1. Introduction

With the high demand for energy along with the depletion of conventional energy sources, development of new energy sources and improved utilization of existing energy sources have become increasingly important.[1] In regard to industrial energy conservation, materials for energy storage and efficiency have attracted the most attention; among these, low-cost phase change material (PCM) has become popular because of its high storage capacity and thermostatic effect during energy storage. PCM can absorb or release heat, change its physical state (e.g. from solid to liquid, and vice versa) and provide latent heat without change in temperature.[2] In order to enhance energy utilization efficiency, PCM has been widely used in air-conditioning, building materials, energy-saving equipment, food preservation and warm supplies, and is regarded as an environmentally friendly energy-saving material.[3-5]

To avoid PCM leakage, PCM is introduced into porous solids to prepare shape-stabilized phase change material (SSPCM) with stable structure. Also, the SSPCM composite can be synthesized by easy and low-cost methods. In Taiwan, the beer breweries discard 4,500 tons of diatomite (DT) every year, and the DT is reused for planting soil or buried in landfill. DT has good adsorbability, stable chemical properties and high porosity; it can adsorb PCM after proper purification pre-treatment. In this study, we purified the recycled DT for adsorbing PCM, and synthesized the SSPCM composite with stable structure, high phase enthalpy, and good thermal conductivity, at low cost.



2. Experiment

2.1. DT purification

For removing the organics and impurities in the DT pores, the recycled DT was calcined and washed by acetone. The purified DT (P-DT) was oven dried, and sieved by mesh screen.

2.2. Synthesis of PEG/P-DT SSPCM

The PEG solution was prepared by PEG600 and PEG1000 in the ratio of 4:1, and the P-DT was then straight dipped in the PEG solution. To observe the structural stability of the PEG/P-DT SSPCM, different PEG/P-DT concentrations (10~50%) were studied in the straight dipping process. The PEG/P-DT mixture was oven dried at 60°C for 30 min, and the dried PEG/P-DT SSPCM with good structure stability was further used in fabricating PCM composites. [6-7]

2.3. Preparation of SSPCM/HDPE composites

PEG/P-DT SSPCM and HDPE were oven dried at 60°C for 1 d before composite fabrication. The composite components, as shown in Table 1, were blended at 170 °C in a counter-rotating internal mixer for 400 s, and then granulated. In the end, the SSPCM/HDPE composites were prepared by compression molding at 170 °C.

Table 1. Formulation of SSPCM/HDPE composites.

Sample	HDPE (g)	SSPCM (g)	MAPE (g)	Al ₂ O ₃ (g)
HDPE	50	-	-	-
PEC	30	12	-	1.5
MPEC	27.6	12	2.4	1.5

3. Results and Discussion

3.1. Physical properties of diatomite

The structure parameters and thermal properties of DT and P-DT are summarized in Table 2. Before purification, the raw recycled diatomite (DT) had a BET surface area of 32.5950 m²/g and pore volume of 0.1277 cm³/g. After purification, the purified diatomite (P-DT) increased the BET surface area and pore volume to 58.2470 m²/g and 0.1788 cm³/g, respectively. Therefore, the calcination and washing treatments successfully removed the organics and impurities inside the DT, and increased the porous space in the end. From the TGA analysis shown in Figure 1, P-DT retains much higher weight than DT after thermal decomposition, indicating that the P-DT is composed of pure inorganic content. Therefore, P-DT can serve as an ideal adsorbent for PEG in the PCM preparation.

Table 2. Physical properties of purified diatomite.

Sample	Structure parameters		Thermal properties
	BET surface area (m ² /g)	Pore volume (cm ³ /g)	Char Yield at 550oC (%)
DT	32.5950	0.1277	87.09
P-DT	58.2470	0.1788	99.05

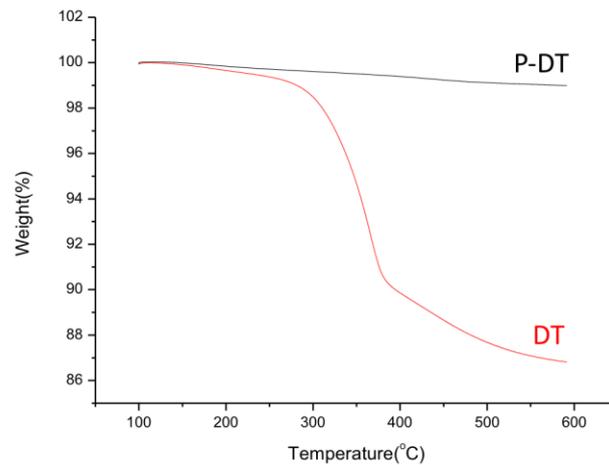


Figure 1. TGA analysis of DT and P-DT.

3.2. Structure stability of PEG/P-DT PCM

As shown in Figure 2, the PEG/P-DT PCM exhibits different structure stability with various PEG contents. The PEG leakage from P-DT was observed after the PEG/P-DT SSPCM was placed in an oven at 60°C for 30 min. In Figure 2(e), the high PEG content resulted in serious leakage, indicating that the P-DT could not adsorb the excess PEG. At 40% PEG content (Figure 2(d)), only 0.2% of the PEG leaked out. With PEG content lower than 30%, the PEG/P-DT PCM forms a stable structure without PEG leakage.

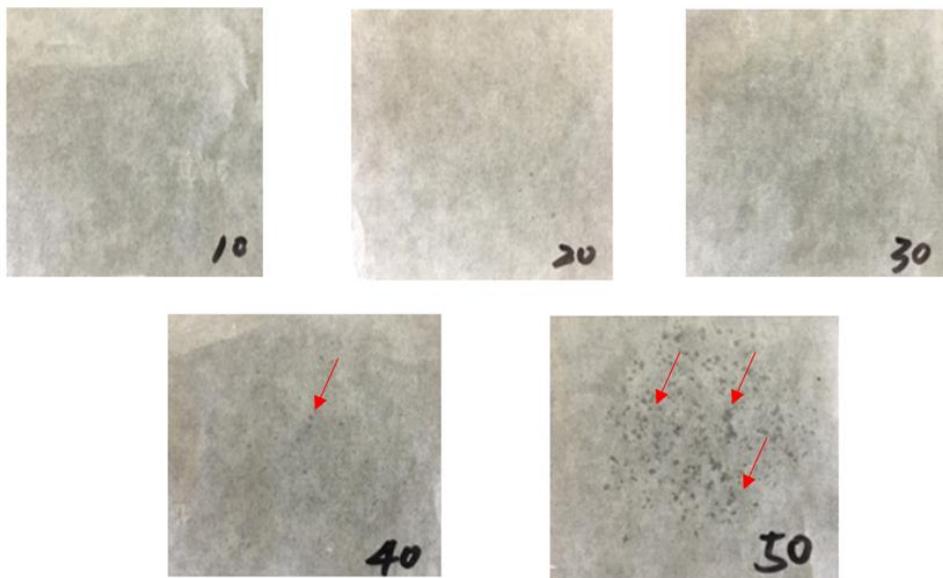


Figure 2. Structure stability of PEG/P-DT SSPCM containing (a) 10% PEG, (b) 20% PEG, (c) 30% PEG, (d) 40% PEG and (e) 50% PEG.

3.3. DSC analysis

The DSC thermograms of PEG and MPEC are exhibited in Figure 3. In Figure 3(a), the PEG consisted of PEG600 and PEG1000 in the ratio of 4:1, and performed phase change from -10°C to 40°C, where

the PEG showed latent heat of 104.9 J/g. The HDPE holds T_m of 133.16°C and enthalpy of 140.2 J/g. After introducing the PEG/P-DT SSPCM, the MPEC exhibited latent heat of 6.741 J/g around 24°C.

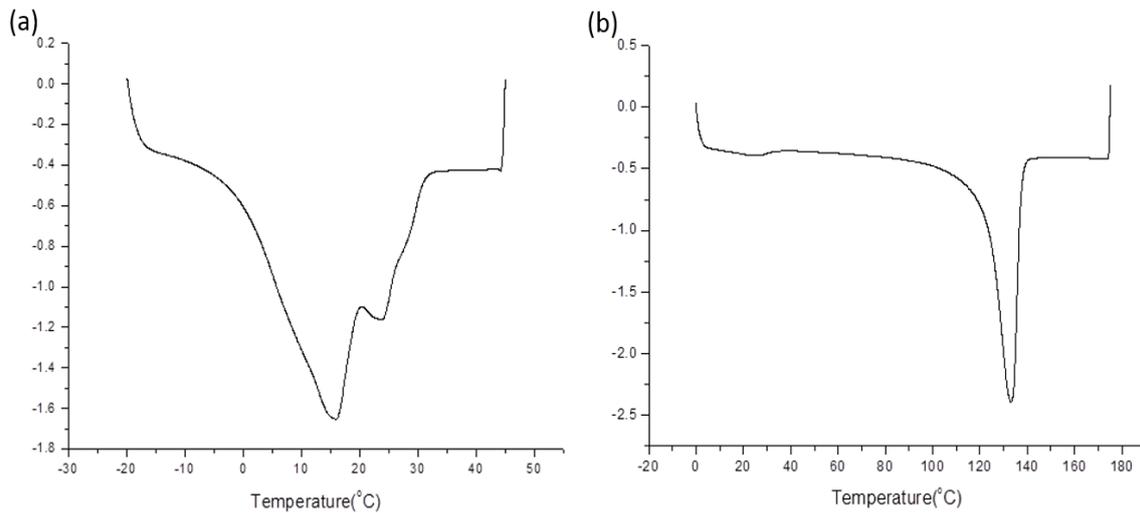


Figure 3. DSC thermograms of (a) PEG and (b) MPEC.

3.4. HDT analysis

The heat deflection temperatures (HDT) of the HDPE and its SSPCM composites are summarized in Table 3. After adding PEG/P-DT SSPCM, the PEC composite elevates the HDT from 75.90°C to 81.77°C because the P-DT porosity can insulate heat and improve thermal resistance. By adding the MAPE for improving the compatibility between the HDPE and PEG/P-DT PCM, the MPEC composite further enhanced the HDT to 89.18°C.

Table 3. Physical properties of HDPE and its SSPCM composites.

Sample	Heat resistance	TGA analysis		Mechanical properties		Thermal conductivity
	HDT (°C)	Td5 (°C)	TMax (°C)	Impact strength(J/m)	Tensile strength(MPa)	k (W/mK)
HDPE	75.90±1.8	432.9	473.0	117.35±2.7	25.25±3.1	0.5196
PEC	81.77±0.4	369.5	403.1 489.1	41.15±1.4	17.75±0.4	-
MPEC	89.18±4.81	386.7	396.2 500.2	34.43±2.4	21.89±0.3	0.6078

3.5. TGA analysis

Thermogravimetric analysis (TGA) and derivative thermogravimetric (DTG) analysis are shown in Figure 4. HDPE has Td5 of 432.9°C. After adding the PEG/P-DT SSPCM, the PEC and MPEC, had Td5 of 369.5°C and 386.7°C, respectively, and the decreasing Td5 was donated by the PEG decomposition at high temperature. From the DTG results, the PEC and MPEC had two TMax peaks.

The first TMax peaks of PEC and MPEC were 403.1°C and 396.2°C, respectively, and were close to the TMax of the PEG (400.1°C). Accordingly, the first TMax peaks of PEC and MPEC were contributed by the PEG adsorbed inside the P-DT. The second TMax peaks of PEC and MPEC were respectively 489.1°C and 500.2°C, and were higher than the TMax of the pure HDPE (473.0°C). The elevation of second TMax peaks resulted from the P-DT and MAPE. P-DT is heat-resistant inorganics, and MAPE can improve the compatibility and thermal stability of PCM composite; therefore, P-DT and MAPE enhanced the second TMax of PCM composites.

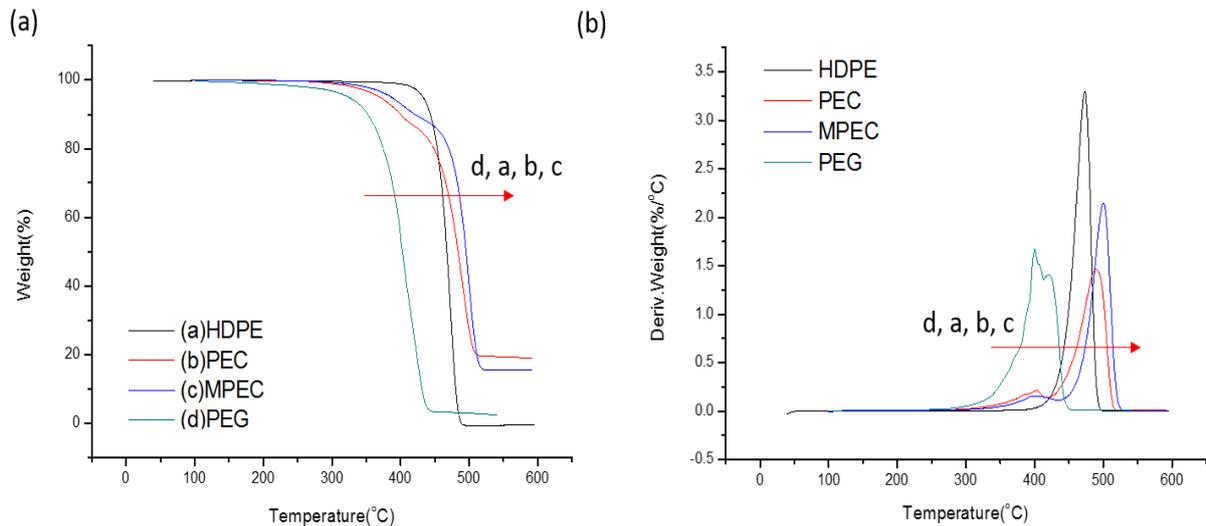


Figure 4. (a) TGA and (b) DTG analysis of HDPE and its SSPCM composites.

3.6. Mechanical properties and thermal conductivity

The impact and tensile strengths are summarized in Table 3. P-DT is a kind of inorganic porous material, so it significantly enhances thermal resistance instead of mechanical properties. HDPE has impact strength of 117.35 J/m and tensile strength of 25.25 MPa. After adding the PEG/P-DT SSPCM, the PEC decreased the impact strength and tensile strength to 41.15 J/m and 17.75 MPa, respectively. By adding MAPE to improve the compatibility and stiffness, MPEC's tensile strength rose to 21.89 MPa.

For quickly conducting heat from environment to SSPCM, Al₂O₃ is employed in MPEC composite. After adding Al₂O₃, the MPEC composite elevated the thermal conductivity from 0.5196 W/mK to 0.6078 W/mK.

4. Conclusion

This study successfully purified recycled DT and functionalized PEG/P-DT as SSPCM material. After purification, the P-DT served as an ideal adsorbent for accommodating PEG with great structural stability. By introducing PEG/P-DT SSPCM into HDPE, the SSPCM/HDPE composites improved the thermal properties like HDT and T_{max}. Other functional materials were also used in the composites, for example, MAPE for better compatibility and tensile strength, and Al₂O₃ for higher thermal conductivity.

5. References

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Acknowledgments

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